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A Study of the Properties of CP: Coefficient of Thermal Expansion, Decomposition Kinetics and Reaction to Spark, Friction and Impact

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ABSTRACT

The properties of pentaamine (5-cyano-2H-tetrazolato-N₂) cobalt (III) perchlorate (CP), which was first synthesized in 1968, continues to be of interest for predicting behavior in handling, shipping, aging, and thermal cook-off situations. We report coefficient of thermal expansion (CTE) values over four specific temperature ranges, decomposition kinetics using linear heating rates, and the reaction to three different types of stimuli: impact, spark, and friction. The CTE was measured using a Thermal Mechanical Analyzer (TMA) for samples that were uniaxially compressed at 10,000 psi and analyzed over a dynamic temperature range of -20°C to 70°C. Using differential scanning calorimetry, DSC, CP was decomposed at linear heating rates of 1, 3, and 7 °C/min and the kinetic triplet calculated using the LLNL code *Kinetics05*. Values are also reported for spark, friction, and impact sensitivity.

Keywords: TMA, CTE, high explosive, energetic materials, CP

INTRODUCTION

The high explosive CP was first synthesized in 1968 by Unidynamics, Inc., Phoenix, Arizona [1]. This was a successful collaboration between Unidynamics and Sandia National Laboratories, Albuquerque, New Mexico, to develop a detonator that employed an energetic coordination compound. In 1977 the first production of CP began and by 1979 the first production of a CP detonator for DOE had been successfully accomplished.

Some 36 years later, scientists are still exploring by use of thermal properties and chemical degradation of CP and other energetic materials to understand properties that affect the use, safe handling, and functional lifetime of the material. Textbook and literature values of various material properties are useful references to experimenters but are often given as singular values at ambient temperatures and pressures. Information such as this does not always suffice for situations such as thermal cook-off where a dynamic temperature-pressure range is involved [2,3].

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This study was conducted to provide data on CP, lot # EL-82936, and to compare the observations to previously analyzed lots of CP. Here we report the coefficient of thermal expansion, CTE (α), of pressed material and the decomposition kinetics calculated from linear heating rates of 1, 3, 7 °C/min. In addition, we measure and calculate the effects that various types of initiation sensitivity tests: drop hammer, spark and friction.

Table 1: Properties of CP [4,5]

Molecular weight	436.98 g/mol
Color	Yellow
Crystal structure	Monoclinic
Crystal density	1.974m/cm ³ x-ray diffraction
Coefficient of thermal expansion, CTE	60 * 10 ⁻⁶ mm/mm°K (298 to 323 K)
Heat capacity	$C_p(\text{cal/g}^\circ\text{K}) = 0.1545$ (353-453 K)
Electrostatic sensitivity	Greater than 20kV at 600pF and 500Ω on loose powder and unconfined pellet

METHODS AND RESULTS

Pacific Scientific of Chandler, AZ manufactured the CP sample material for this study.

COEFFICIENT OF THERMAL EXPANSION

Thermomechanical analysis (TMA) measures linear or volumetric changes as a function of time, temperature and force [6]. It can provide a better understanding of physical properties such as glass and solid-solid phase transitions. Most analyses are presented in the form of the coefficient of thermal expansion:

$$dL/(dT * L_o) = \alpha \text{ (coefficient of thermal expansion)} \quad (1)$$

where dL is the change in length (μm), dT is the change in temperature (°C), and L_o is the initial length (meters).

We measured the CTE of CP using a TA Instruments Model 2940 TMA that was controlled by a TA 500 Thermal Analyzer. A TMA Mechanical Cooling Accessory, manufactured by TA Instruments, controlled the temperature. A quartz micro-expansion probe was used for all samples with a force of 0.01 Newtons (N). Ultra high purity nitrogen carrier gas was used at a constant flow rate of 100 cm³/min. Samples were heated at a linear heating rate of 3 °C/min.

Temperature, force, probe and cell constant calibrations were carried out as prescribed [7], using indium, lead, tin and zinc metals along with aluminum standard reference material.

Coefficient of thermal expansion measurements using a certified aluminum standard had less than $\pm 2\%$ errors associated over the temperature range of -20 to 65°C .

Our CP sample was uniaxially pressed at room temperature in a compaction die using a single pressing cycle of 10,000 psi. Table 2 gives the measured sample mass, volume, density and dimensions used for this experiment. Comparison to the theoretical maximum density (TMD) [8] indicated the sample achieved 85.7% TMD.

Table 2: Sample mass, volume, density and dimensions

Material	length, cm	diameter, cm	mass, g	volume, cc	density, g/cc
CP	0.089	0.508	0.306	0.0180	1.696

Figure 1 shows a plot of dimensional change versus temperature. CTE values were calculated using equation 1 and are listed in Table 3 for six specific temperature intervals. The errors associated with this experiment range from 2-16 parts in 100.

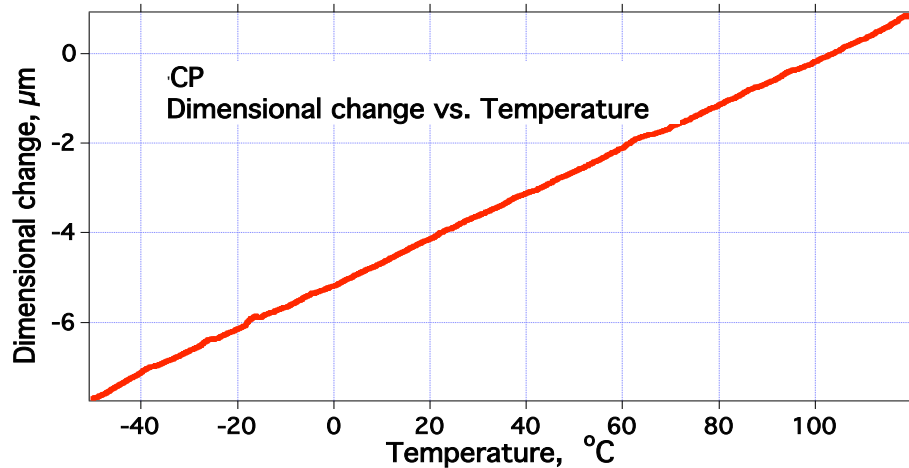


Figure1: CP Dimensional change versus Temperature

Table 3: CP CTE values, α , $\mu\text{m}/\text{m}^\circ\text{C}$

Material	-20°C to 0°C	0°C to 25°C	25°C to 50°C	50°C to 75°C	75°C to 100°C	100°C to 125°C
This work	59	55	59	56	55	62
Lit. value [9]	58	59	60	62	66	71

DECOMPOSITION KINETICS

We determined thermal decomposition kinetics using differential scanning calorimetry (DSC). DSC measures the difference in the heat flow between a sample and an inert reference measured as a function of time, where both the sample and reference are subjected to a controlled environment of time, temperature, and pressure; the rate of reaction is assumed to be

proportional to the excess heat flow over that expected from simple heat capacity. DSC analyses of CP were carried out using a TA Instruments Model 2920 and Perkin-Elmer aluminum pan that had a small pin-sized perforation to allow generated gases to escape during decomposition. Samples sizes were limited to <0.2 mg to prevent bursting the pan. Linear heating rates of 1, 3, and 7 °C per minute and a purge flow of 50 cm³/min of ultra high purity nitrogen were used. Data was analyzed using the LLNL kinetics analysis program *Kinetics05*.

Chemical kinetic analysis is full of pitfalls for complex reactions. The basic starting equation gives the rate of reaction in terms of a rate constant times a function of the extent of reaction:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where the temperature dependence of k is typically described by an Arrhenius law ($k=A\exp(-E/RT)$), where A is a frequency factor, E is an activation energy, and R is the gas constant.

One of the simplest, yet generally reliable, methods of kinetic analysis is Kissinger's method [10], in which the shift of temperature of maximum reaction rate (T_{max}) with heating rate (β) is given by

$$\ln(\beta/T_{max}^2) = -E/RT_{max} + \ln(AR/E). \quad (3)$$

The CP reaction rate profile has a very sharp peak, and this method yielded $A=3.13 \times 10^{14} \text{ s}^{-1}$ and $E=42.9 \text{ kcal/mol}$, with a standard error of 2.0 kcal/mol on the activation energy.

The reaction profile width is only 18% of the peak width of a first-order reaction, so it is definitely some type of autocatalytic or shrinking core mechanism. In addition, the reaction has leading and trailing shoulders, indicating multiple processes. An increasingly common method of analyzing such a complex reaction profile is some type of isoconversional method, and we use Friedman's method here, in which an effective 1st-order k is determined at each percent of conversion by dividing the measured rate by the fraction converted and fitting the resulting rate constant at extent of conversion to an Arrhenius law [11]. The result is a measure of A and E as a function of conversion, as shown in Figure 2 for our CP data.

A comparison of measured and calculated reaction rates is shown in Figure 3. Sensitivity to baseline selection in combination with the extremely sharp reaction profile causes some minor problems with the method. A similar isoconversional analysis by B. Roduit of AKTS yielded very similar A and E parameters up through 90% conversion, but both A and E then plunged towards zero above 90% conversion. The AKTS software has a baseline optimization feature,

which introduces a difference from our analysis for this region of the reaction. The difference makes little practical difference, however, since the material is nearly spent by that point.

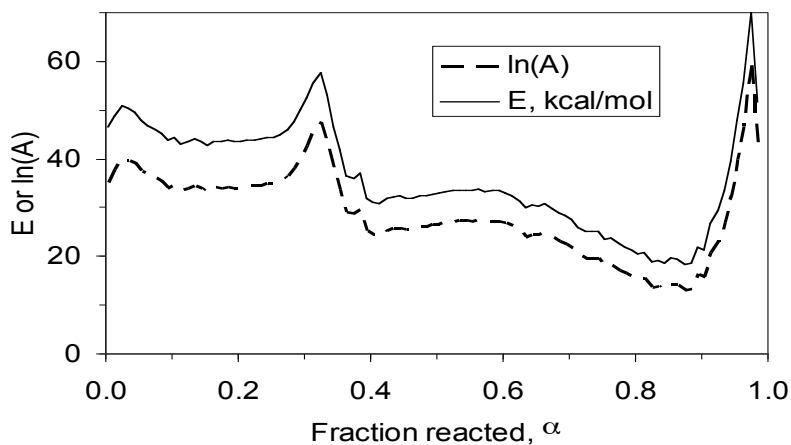


Figure 2: Conversion dependence of A and E determined by Friedman's method.

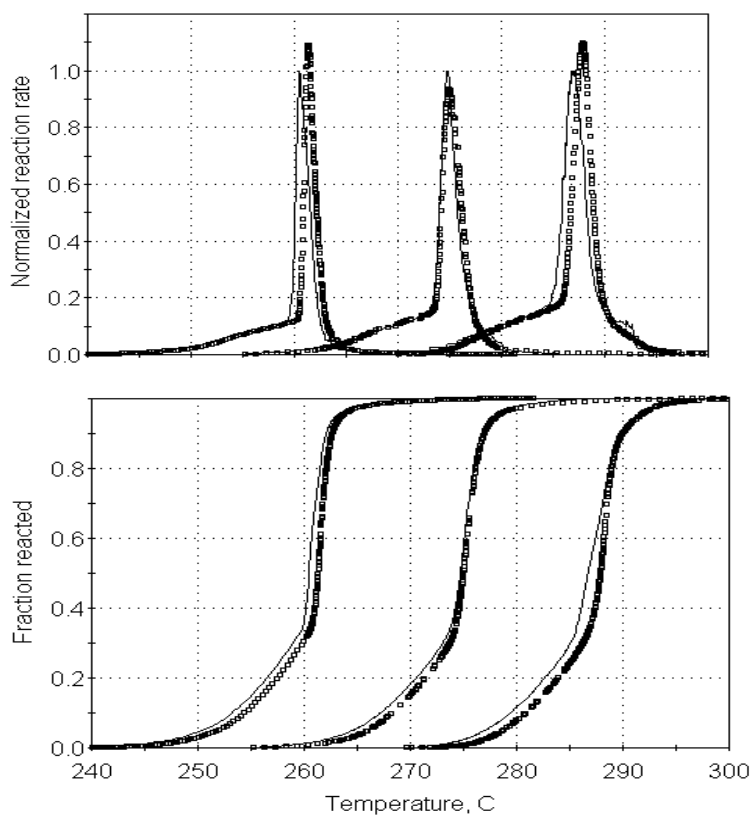


Figure 3: Comparison of measured and calculated reaction rates and fractions reacted for Friedman's method.

REACTION TO VARIOUS STIMULI

Small scale testing of energetic materials and other compounds is done to determine sensitivity to various stimuli, including friction, impact and static spark. These tests are of monumental importance for several reasons, but mainly to establish parameters for the safety in handling and carrying out experiments that will describe behavior of materials that are commonly stored for long periods of time. This report will include the existing tests often referred to as drop hammer (impact sensitivity), friction, and spark. The accumulated data will be discussed in this document.

Friction sensitivity

The frictional sensitivity of CP was evaluated using a B.A.M. high friction sensitivity tester. The tester employs a fixed porcelain pin and a movable porcelain plate that executes a reciprocating motion. Weight affixed to a torsion arm allows for a variation in applied force between 0.5 and 36.0 kg, and our tests used a contact area of 0.031 cm². The relative measure of the frictional sensitivity of a material is based upon the largest pin load at which less than two ignitions (events) occur in ten trials. No reaction is called a “no-go”, while an observed reaction is called a “go.” CP was observed to have 1/10 “goes” at 1.0 kg at 68°F and a relative humidity of 60%. CP was compared to an RDX calibration sample, which was also found to have 1 event in 10 trials at 12.4 kg. This material is considered to be friction sensitive.

Spark sensitivity

The sensitivity of CP toward electrostatic discharge was measured on a modified Electrical Instrument Services Electrostatic Discharge (ESD) Tester. Samples were loaded into Teflon washers and covered with a 1-mm thick Mylar tape. The density of this packed material was 1.4 cm³/g. The ESD threshold is defined as the highest energy setting at which a reaction occurs for a 1 in 10 series of attempts. Tests were run on powder and pellets at 68°F and a relative humidity of 56%. No reactions were observed (0/10) at 10 kV (1J). This material is not spark sensitive under these specific conditions.

Impact sensitivity (drop hammer)

An Explosives Research Laboratory Type 12-Drop Weight apparatus, more commonly called a “Drop-Hammer Machine” was used to determine the impact sensitivity of CP relative to the primary calibration materials PETN, RDX, and Comp B-3 at 68°F and 56% relative humidity. The apparatus was equipped with a Type 12A tool and a 2.5-kg weight. The 35-mg ± 2-mg powder sample was impacted on a Carborundum “fine” (120-grit) flint paper. A “go” was defined as a microphone response of 1.3 V or more as measured by a model 415B Digital Peakmeter. A sample population of 15 was used. The mean height for “go” events,

called the “50% Impact Height” or Dh_{50} , was determined using the Bruceton up-down method. The Dh_{50} for CP for this experiment was 60.6 ± 1.0 cm. For comparison, the Dh_{50} of PETN, RDX, and Comp B-3 were measured at 15.5, 34.5, and 41.4 cm, respectively.

DISCUSSION

Our CP thermal expansion values as a function of temperature agree with the only previous report known to us [9]. The comparison of CP, PETN, HMX and RDX in Table 4 shows that CP’s CTE values are basically constant over the temperature range of -25°C to 75°C . CP’s values are the lowest of this set of energetic materials except at -25°C where HMX is approximately 39% less. PETN’s CTE starts approximately 40% higher than CP, and its CTE increases approximately 11% over the temperature range. HMX and RDX molecular structures are well known and have been studied extensively in the past. Both HMX and RDX CTE’s almost double over the dynamic temperature range of -25°C to 75°C .

Table 4: CTE values ($\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$) for CP, PETN, HMX and RDX.

Temperature, $^{\circ}\text{C}$	CP	PETN	HMX	RDX
-25	57	82	35	49
25	57	88	49	65
75	56	91	82	96

Searcy and Shanahan [13] report that decomposition of CP occurs as a three-step mechanism where step 1 is the dissociation of the ammonia ligand, and is an endothermic process. Step 2 is the oxidation of the ligand around the cobalt atom by the perchlorate ion. Step 3 is the oxidation of the residual solid products by the perchlorate ion. This reaction sequence accounts for the complex reaction profile we observe. The third step can be very rapid, as is indicated by the sharp reaction peak in Figure 3. In related thermogravimetric experiments at $20^{\circ}\text{C}/\text{min}$, using a few tenths of mg, we reproducibly observed a weight “gain” from the explosive impulse followed by complete mass loss over a 15 s interval.

Two reaction characteristics of interest are the peak reaction temperature for a given heating rate and the activation energy, which describes how it shifts with a change in heating rate. Massis et al. [11] report that sealed samples decompose about 50°C higher in temperature compared to open samples. The decomposition temperatures reported here for pierced pans agree well with those for open pans reported by Massis et al., while the results of Burnham et al. [14] and Massis et al. for hermetically sealed pans agree well with each other when differences in heating rate are taken into account.

Using Kissinger’s method [9], Massis et al. [11] report a range of activation energies from 39.2 kcal/mol to 49.6 kcal/mol based on impurity that is described as an amide complex, our results of 42.9 kcal/mol falls somewhere in the middle of that range. Massis et al. contend that varying amounts of amide complex impurity causes the activation energy to shift and

therefore one can estimate the stability. They also observe that gaseous decomposition products such as ammonia appear to inhibit the decomposition by shifting the reaction to higher temperatures. Listed below in Table 5 are activation energy values reported by Massis et al. from open pan and hermetic pan experiments, and they are compared to activation energy determined here and that reported by Burnham et al. [14]. There are no clear trends in the activation energy as a function of amide complex content, so we can merely say that our results lie within the range of literature values. Since there has not been much testing of lot #EL-82936, this report therefore lays a baseline for this specific lot of CP. We did not do any impurity analysis on this material, and there could be unknown impurity contributions to the activation energy.

Table 5: Activation energy (kcal/mol) of CP with varying amounts of amide complex impurity. Experiments are non-isothermal unless otherwise noted.

Sample configuration	Lot 36353A [10] 0.9 – 1.0 %	Lot 47344 ~ 4 %	Lot 36164 8 – 10 %	Lot 82936 Amide complex % unknown
Open [11]	44.4	49.6	39.2	---
Open (iso) [11]	43.4	42.9	41.7	---
Perforated pan (this work)	---	---	---	42.9
Hermetic pan [11]	34.4	43.7	42.1	---
Hermetic pan [14]	---	---	---	47.1

The methods and apparatus used for drop hammer, spark and friction tests have been recorded in this report so that other experimenters can compare our results to others with reference to these procedures. Listed below in Table 6 are reported literature values and values observed in this work that clearly reflect the differences in testing apparatus.

Table 6: Summary of safety test results

Test	CP, literature [15]	This work
<i>Friction</i> (fine)	30 psig @ 8ft/s, 180 psig @ 3ft/s	455 psig @ 0.1 ft/sec
<i>Friction</i> (coarse)	< 30 psig @ 8ft/s 420 psig @ 3ft/s	-----
<i>ESD threshold</i> (J)	^a 0.165 (fine) 0.326 (coarse)	> 1.0
<i>Dh</i> ₅₀ (cm)	19 (fine) 9 (coarse)	61
<i>E</i> (kcal/mol)	39.2-49.6	42.9

^a: Samples were approximately 35 mg in mass; no density or sample dimensions are available.

Our CP sample appears to be more sensitive to friction than the Indian Head results when the drag velocity is taken into account. Our drop hammer height is higher (lower sensitivity). This could be because our sample is finer by comparison to their particle-size trend. Overturf [16] reports that our sample has a specific surface area of $0.573 \text{ m}^2/\text{g} \pm 0.02 \text{ m}^2/\text{g}$, but there is no surface area reported for the Indian Head samples. Indian Head report particle sizes of 70-90 μm for the fine powder and 100-200 μm for the coarse powder, which results in smaller calculated surface areas. Using a Zeiss microscope we measured CP particles in the 5-20 μm range (see figure 4), which confirms that our powder is finer than either Indian Head powder. Our ESD threshold is higher (less sensitive) even though our particle size is smaller, which should cause the threshold to decrease [16]. This may be due to the electrical pulse that is delivered to the sample.

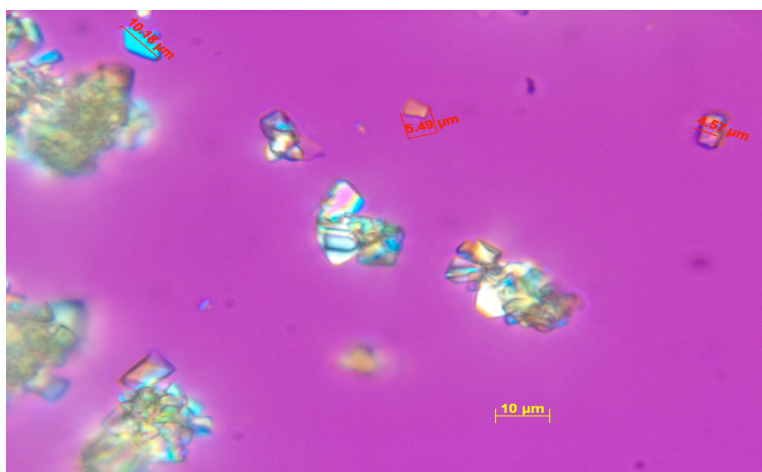


Figure 4: CP lot EL-82936

We have determined that CP, lot EL-82936, compares fairly well to other known CP material. In making this assessment, it became obvious that existing data should be compiled in a more accessible format. Also, future plans should consider bringing all laboratories that have a need for understanding the stability of CP together to discuss unification of testing methods. This will not only bring analyses and results in-line, but it will also insure that a better understanding of the stability of an energetic material such as CP is safe for all that are exposed to its handling, operation or use.

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